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Magnetic nanoparticle characterization using nano-SQUID based on niobium Dayem bridges

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Abstract

Magnetic nano-sensors based on niobium dc SQUID (Superconducting Quantum Interference Device) for nanoparticle characterization are presented. The SQUIDs consists of two Dayem bridges of 90 nm x 250 nm and loop area of 4, 1 and 0.55 μm^2. The SQUIDs were designed to have a hysteretic current-voltage characteristic in order to work as a magnetic flux-current transducer. Current-voltage characteristics, critical current as a function of the external magnetic field and switching current distributions were performed at liquid helium temperature. A critical current modulation of about 20% and a current-magnetic flux transfer coefficient (responsivity) of 30 $\mu A/\Phi_0$ have been obtained, resulting in a magnetic flux resolution better than 1 $m\Phi_0$. In order to show the effectiveness of sensor for nanomagnetism applications, we performed measurements with and without magnetic nanoparticles on the SQUID loop applying a magnetic field parallel to the SQUID plane. In this configuration the magnetic flux coupled to the SQUID is mainly due to the presence of magnetic nanoparticles. The magnetic nanoparticles can be easily detected and their response to magnetic field studied.
Measurements has been performed on Fe_3O_4 nanoparticles prepared by thermal decomposition method with a nominal particle size of 8 nm. Some examples of magnetization measurements were recorded at low temperature after Zero Field Cooling.

Keywords: Superconductivity, SQUID, Dayem nanoBridge, Magnetic Nanoparticle, Magnetic sensor

1. Introduction

Over the past years the synthesis and application of nanostructured materials have made a considerable progress. Magnetic nanostructured (1–100 nm) systems cover a wide range of applications, from ultra-

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high-density electronic data-storage media to high strength permanent magnets, from new magnetic superconductors to nanobiomagnetic sensing strategies[1] .

One of the trends taken by spintronics envisages molecules as possible end points in the race toward miniaturization[2,3]. The Molecular spintronics focuses on the reading and manipulation of molecular spin states by electrical currents in miniaturized devices made of one or a few molecules[4].

When the dimension of the material is below some critical radius R_0 (typically in the range from 10 to 25 nm), the fraction of near-surface atoms is strongly increased as compared to bulk materials and the effect of the crystal lattice disorder near the surfaces plays an important role in the material properties that can differ markedly from those of the bulk material [5,6]. For this reason the study of fundamental magnetic parameters of magnetic nanoparticles is both of practical and theoretical interest.

While the determination of fundamental parameters of bulk materials does not pose serious difficulties, this problem is not simple for nanoparticles and several approaches have been proposed[7-8].

Between them the using of a SQUID (Superconducting Quantum Interference Device) seems to be a very promising one and several novel SQUID-based techniques have emerged to characterize the magnetic nanoparticles and to measure of the magnetic response of individual molecules[9].

For this application, the device sensitivity scales as the side length of the SQUID loop, therefore in the last years there is a growing interest in the development of SQUIDs having a sub-micrometric loop diameter (100-200 nm), in order to measure the magnetic nano-objects [10-15]. In such a way, it has been possible to reach a spectral density of magnetic moment noise as low as few $\mu_B/Hz^{1/2}$ ($\mu_B = 9.27 \times 10^{-24}$ A m^2 is the Bohr magneton) referred to a sensor geometrical area of about (200 x 200) nm^2 making such nano-sensors ideal for local magnetic measurements. The magnetization change ΔM of magnetic nano-particles coupled to the SQUID system can be related to the variation of the magnetic flux $\Delta\Phi$ threading the SQUID's loop, through a coupling factor α, $\Delta\Phi=\alpha\Delta M$, α depending on both geometry and relative position of SQUID and particles [16-19], therefore successful methods based on chemical or microscopic techniques have been devoted to finely arrange the nano-particles within the sensor loop or very close to it [20-22]. Recently it has also been developed a scanning magnetic microscope including a nanoSQUID fabricated on the apex of a sharp quartz[23]. It is a highly promising probe for nanoscale magnetic imaging and spectroscopy.

A nano-SQUID sensor requires deep sub-micron Josephson junctions which are provided by two Dayem nano-bridges (nano-constriction of a superconducting film) fabricated by using Electron Beam Lithography (EBL) or Focused Ion Beam (FIB) having a length and a width comparable to the coherence length. Furthermore, with respect to the tunnel junctions, Dayem bridges are almost insensitive to the magnetic field applied in the plane of the SQUID loop (up to few Tesla). The lack of sensitivity to a high field applied in the SQUID plane is a necessary request for the measurement of the nanoparticles magnetization.

Nanoscale SQUIDs having loop diameters of order 1 μm or smaller using Nb nanobridge junction fabricated by electron beam lithography, showing flux noise of 2-5x10^{-6} $\Phi_0/Hz^{1/2}$ at 4,2 K have been reported in ref. [24,25] . NanoSQUIDs based on Nb nanocostriction produced by focused ion beam have been reported showing a flux noise of 1.5x10^{-6} $\Phi_0/Hz^{1/2}$[25] . Recently Nb nanoSQUID with a loop size of 350 nm operated at T<10K , using a cryogenic SQUID series array pre-amplifier, showed a system noise of 0.2x10^{-6} $\Phi_0/Hz^{1/2}$[26]. Recently, preliminary measurement of magnetization from ferritin and FePt nanoparticles attached to a 200 nm hole nanoSQUID have been performed [22,27]. All mentioned sensors exhibit a non-hysteretic current voltage characteristic allowing to employ the device as magnetic flux-voltage transducer. Even if the most applications employ the SQUID sensors as a magnetic flux-voltage transducer, in the case of nano-magnetism investigations, the SQUIDs are typically used as magnetic flux-current transducer [29]. In this case, the sensors show a hysteretic current–voltage characteristic and the measurement method consists in measuring the critical current of the device.

As the critical current I_c is a periodic function of the flux going through the SQUID loop, one can easily deduce the flux change in the SQUID loop by measuring the critical current.

In this paper, we present SQUID sensors based on single layer Nb nanobridges produced by EBL technology and having an hole length ranging from 2 μm to 0.75 μm. The sensors show a hysteretic characteristic and thay are used as a magnetic flux-current transducer; in this operation mode the sensor performance is reliable, reproducible and it can be operated at temperature below 4.2k.

The preliminary measurements of iron oxide nanoparticles show the effectiveness of such sensor to study the magnetism of nanoparticles.

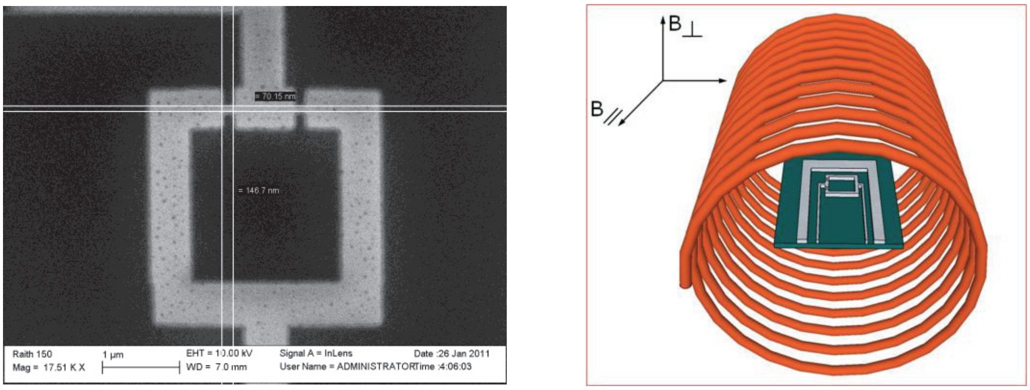

Figure 1 a) The SEM image of a Nb NanoSQUID with a 2 micrometer loop: the nanobridges are about 150nm long and 70nm wide. b) Schematic of the measurement principle: the chip is inserted in a solenoid providing a magnetic field parallel to the SQUID plane, the integrated coil generates a magnetic field suitable for the nanoSQUID characterization.

2. Material and methods

The main requirement for a SQUID designed to detect magnetic nanoparticles is a very small SQUID loop area. Ideally, to gain the best coupling factor, the loop size should be comparable to those of the nanoparticle directly coupled to it. The two superconducting Dayem nanobridges consist of narrow constrictions in the plane of the thin film. The two opposite sides of the constriction are weakly linked and when the constriction dimension is sufficiently small (of the order of the coherence length ξ,) the structure exhibits periodical current-phase relationship[16] and high current density. Nanobridge fabrication is relatively easy and just requires single process step. Our fabrication is based on a lift-off process: a 20 nm Nb film is deposited at room temperature by dc magnetron sputtering on a silicon substrate previously coated by resist. The use of polymethyl methacrylate (PMMA) as electron beam resist, exposed to a l0KV e-beam, provides the typical overhang profile in the resist thickness needed to obtain a good lift-off. After the lift off in acetone, a layer of Flowable Oxide (Fox-22 DOWCorning) is spinned coated to obtain a passivation layer to protect the nanostructure.

This process is based on simple and reliable steps resulting a very high yield. Loop diameters ranging from 750 nm to 2 μm and bridges with a width *w* ranging from 50 nm to 80 nm and a length *l* ranging from 50 nm to 250 nm have been designed and produced. The SEM image of a device with a loop size of 2 μm is shown in Fig. 1(a). On a single die of 100 mm^2 area were fabricated 12 nano-SQUIDs with integrated bias coils.

The electrical transport properties of the nanoSQUIDs and the preliminary detection of magnetic nanoparticles have been performed at a temperature of T=4.2 K in an electro-magnetically controlled environment. An uniform magnetic field parallel to the plane of the SQUID has been provided by an external solenoid surrounding the device (figure 1b). A field perpendicular to the SQUID loop, used to characterize the SQUID, is provided by an integrated coil. The current-voltage (I-V) characteristics of the device have been measured with a battery powered low-noise room temperature electronics. A typical hysteretic I-V curve is shown in the inset of Fig. 2; This hysteretic I-V curve made it impossible to use standard read out SQUID electronics. Therefore to measure the nanoparticles magnetization we used the SQUID as a magnetic flux-current converter. The probability of switching out from the superconducting state at T = 4.2 K is mainly due to thermal fluctuation giving origin to the critical current distribution reported in figure 2a. The value of the critical current used for the magnetic measurement has been determined averaging over a relative large number of switching events (usually between 1000 and 100000) therefore measuring the switching current probability distribution of the SQUID[30]. Typical critical current values of 100 μA are obtained and they can be measured with an instrumental error of 1 part to 10^4 [31] . A typical magnetic pattern of a nanoSQUID is reported in figure 2b. The data have been obtained as mean value of 10000 critical current switchings and they has been measured as a function of the applied magnetic flux provided by the integrated Nb coil. The pattern is used to determine the SQUID modulation and responsivity $\partial I_c/\partial \Phi$ and to choose the best operating point: in the present work a modulation of about 20% and a responsivity up to $32\mu A/\Phi_0$ have been obtained.

The Fe_3O_4 magnetic nanoparticles (MNPs) were synthesized by thermal decomposition in the presence of oleic acid and oleylamine as surfactants and organic solvent with high boiling point [32,33]. The X-ray diffraction pattern of the powder indicates the presence of a unique Fe_3O_4 phase with a cubic spinel structure (PDF Card 22-1086). Using Debye-Scherrer formula on [400] reflection an average crystallite size of 7.2 nm is obtained. TEM analysis confirms that the synthesis procedure leads to the formation of essentially spherical and uniform nanoparticles with diameter log-normal distributed (<D>TEM= 7.3 nm). The presence of oleic acid at the nanoparticle surface keeps them isolated from each other by a coating layer of about 2 nm [34]. The nanoparticles were diluted in cyclohexane and a drop of solution was put on the chip. After the solvent evaporation a uniform coating of MNP was covering the whole chip resulting in approximately 10^5 particles on the SQUID loop of 1 μm.

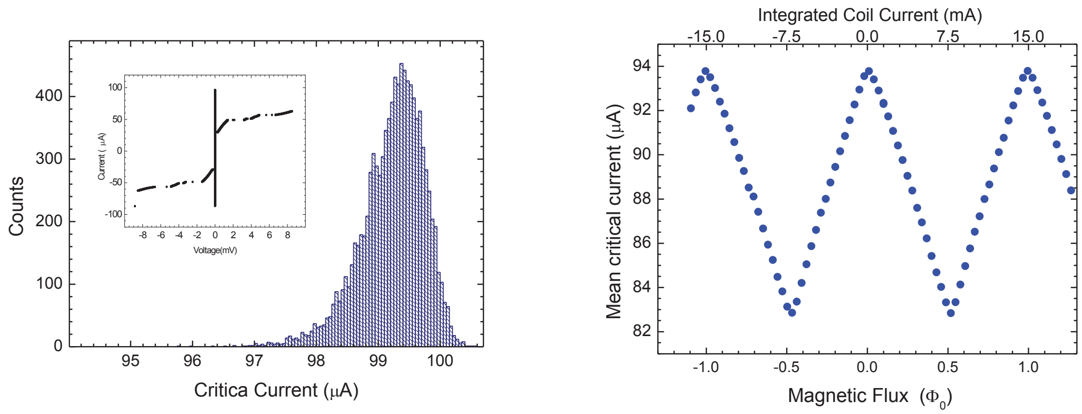

Fig.2 (a) Critical current distribution of a nanoSQUID having 1 μm loop obtained recording 10000 switching events. Inset: a typical hysteretic IV characteristic. (b) The magnetic pattern of a 2 μm loop nanoSQUID obtained averaging 10000 switching events and using the niobium integrated coil to provide the magnetic field perpendicular to the loop plane

3. Results and Discussion

The flux concatenated to the SQUID loop in absence of MNPs is directly proportional to the current coil (reported on the top horizontal scale of figure 2b) and it is possible to determine the value $\partial\Phi/\partial I_{coil} = \Delta\Phi/\Delta I_{coil}$ that can be used to compensate the magnetic flux in the SQUID loop in order to keep the SQUID at is optimal working point.

It is worth to note that when the critical current measurements are performed in presence of the magnetic field parallel to the SQUID loop, the SQUID response is negligible. In the case that the sample is not perfectly aligned to the solenoid axis the magnetic field has a small component perpendicular to the SQUID plane and a few amount of magnetic flux can concatenated to the SQUID giving origin to a modulation similar to the one reported in fig. 2b. In the latter case a small hysteresis in the pattern may also appear due to the pinning of some fluxons trapped in the superconducting film. The alignment has been optimized in order to minimize this effect to a level that does not affect the measurement of magnetic properties of MNPs.

The same measurements were performed after the SQUID was covered by MNPs: the critical current distribution and the magnetic pattern obtained using the magnetic field provided by the integrated coil were not appreciably affected by the presence of MNPs. However when the measure of the average critical current were repeated as function of the magnetic field generated by the solenoid, the presence of MNP could be easily detected by the change in periodicity of the pattern as reported in figure 3a.

At beginning of the measurement reported, the MNP particles were magnetized at -70mT and magnetic field was then varied by discrete step of +1mT up to 70mT and the critical current distribution measured for each step (full circle in the figure). The magnetic flux concatenated to the SQUID loop changed quite slowly at the beginning of measurement and a variation of about 50mT was needed to couple a single flux quantum from the SQUID loop. After crossing the zero of the magnetic field, the flux concatenated to the loop started to change more quickly and about 20mT were sufficient to change the concatenated flux of Φ_0. Once the magnetic field reached 70mT it was reduced by step of 1mT down to -70mT recording the average critical current (empty square in the figure) and the same behaviour was recorded.

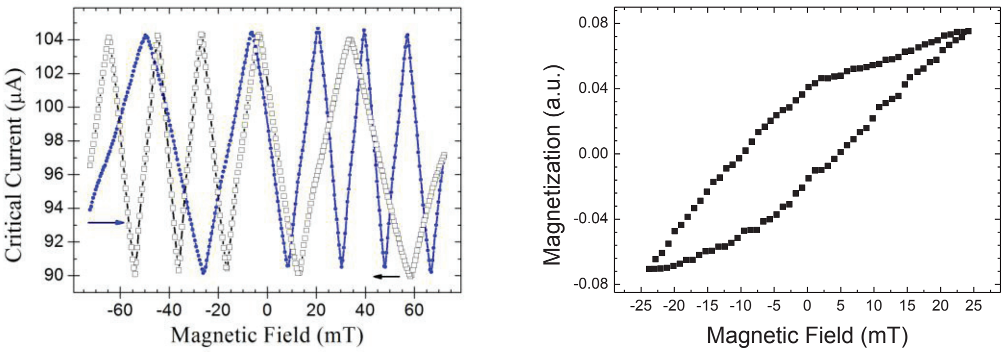

Figure 3 (a) Magnetic pattern recorded by a nanoSQUID of 1micron loop in presence of MNP: the measurement starts at -70mT (full dots) and reaches 70mT, the empty squares represent the reverse direction (from 70mT to -70mT). The hysteresis in the scanning direction can be deduced by the change in period. (b) The magnetic flux can be compensate from small magnetic field making the presence of the hysteresis more clear. The Y axis is proportional to the magnetization trough the coupling flux α

The change of the SQUID response as function of the applied magnetic field is a clear indication that the flux concatenated is not proportional to perpendicular component of the applied field but there is an additional contribution due to magnetization of MNPs. The magnetic flux due to the MNPs was too large to be compensate at this magnetic field, an example of an hysteresis recorded at lower field for a 2micron SQUID loop is reported in figure 3b.

Conclusions and perspectives

We realized integrated magnetic sensors based on hysteretic niobium dc SQUID for magnetic nanoparticle characterization. The SQUIDs were designed to be employed as a magnetic flux-current transducer. A current-magnetic flux transfer coefficient (responsivity) of 30 $\mu A/\Phi_0$ and the intrinsic magnetic flux resolution of about 0.3 $m\Phi_0$ have been obtained. We performed measurements with iron oxide nanoparticles on the SQUID loop showing that the presence of magnetic nanoparticles can be easily detected and the hysteresis loop measured, indicating that the sensor can be effectively used in nano-magnetism applications. We intend to implement the compensation of the magnetic flux treating the SQUID loop to record magnetic hysteresis loop at higher magnetic field in order to measure the magnetic behaviour of Fe_3O_4 MNPs having different dimensions and to investigate other magnetic materials.

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